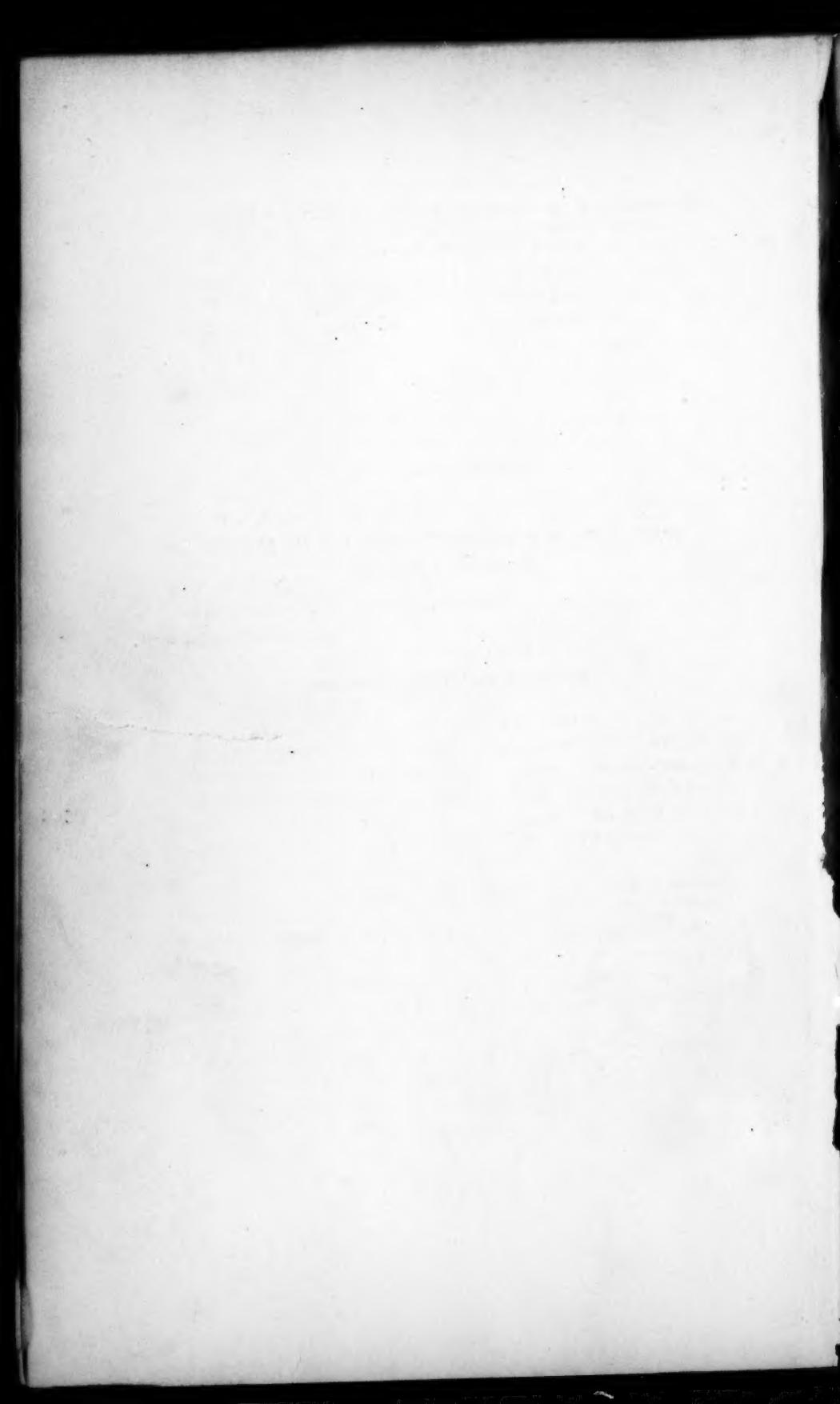


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ATOMIC VOLUME.*

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COMPRESSIBILITY is a universal property of matter. It is so essential an attribute of the experimental universe that it is ascribed even to the imponderable and imaginary ether as well as to "material." The three states of matter are compressible in very varying degrees, dilute gases being compressible to a great extent, highly compressed gases and liquids to a far less extent, and solids to an extent usually even less than liquids. The first case has been studied in great detail, the last two scarcely at all.

Compressibility is simply an evidence of work done upon a system by a given pressure. If the application of considerable pressure in a system causes only a slight change of volume, it is evident that there must be other powerful influences at work. Clearly a clue as to the variation in these influences can be found in the quantitative study of the phenomena.

In all reversible cases which may be studied directly, an increase in pressure is accompanied by an increase of resistance to pressure and a diminution of volume. This depends upon the fundamental idea of equilibrium, and is a special case of the general principle sometimes named after Le Chatelier. Working backwards from this idea, one may infer with regard to any given substance at a given temperature, that it is under the influence of great pressure if its volume-change is unusually small under addition of a given pressure.

There are two conceivable causes of great compression in a substance. The pressure may be applied from the outside, or it may be due to the mutual internal attraction or affinity of the smallest particles of the substance for one another. That is, the substance may be compressed either by an outside pressure, or by the intensity of its own cohesion. The first may be typified by highly compressed gases, the second by liquids, whose small compressibility may be taken as evidence of great compression.

In solids one must consider also the directive agency which manifests itself in crystalline form and optical structure. In a few cases the "crystallogenic force" seems to be rather directive than attractive; in other cases it seems to have both properties, for considerable diminution in volume may occur. The presence of the crystal-making force complicates the phenomena and is a considerable stumbling-block in the way of the study of the internal tension of solids.

In view of these facts, it seemed to me possible that the study of compression as manifested by atomic volume under different circumstances, as well as of atomic compressibility, might afford some light as to the affinities at work. The attempt, while only just begun, has not been wholly unsuccessful.

Evidently the liquid is the most suitable state in which to study the effects of molecular and atomic compressibility. It is most suitable because the irregularities in the behavior of liquids are very great, indicating various internal stresses, and because they are nevertheless not at the mercy of the directive crystal-making tendency which superposes its own influence upon that of cohesion. The great difficulty in the subject lies in the fact that the total compressibility of a substance is usually made up of a number of parts; the molecular compressibility might be due partly to a diminishing of the so-called "free-space" between the molecules, as well as to a diminishing of the distance between the atomic centres. In words free from hypothesis, we may say that the compressibility may be made up of a chemical and a physical compressibility. When one comes to compute from compressibility the probable affinities, one is still more at a loss,—for each affinity is a mutual affair, concerning two specific substances. The immense number of variables thus introduced has discouraged most investigators, and I can find little if any hint of the significance of chemical compressibility in the literature familiar to me.*

In a case of this kind, one naturally seeks at first cases as simple as possible. A study of the volume changes which take place on mixing liquids reveals at first no apparent regularity. In some cases an expansion occurs, but more usually a contraction; sometimes heat is evolved, and at other times heat is absorbed. One law may, I think, be detected in the midst of the confusion, namely: *Similar liquids exhibit less change of volume on mixing than dissimilar ones do.* That is, where the

* The considerations of Nordenskjöld are too seriously complicated by uncertain assumptions to have much value. (See Ostwald's *Lehrbuch*, I. 850 (1891), for these and similar considerations.)

affinity of a substance for itself is not unlike that of the substance for another, no great contraction or expansion occurs on mixing. Thus benzol and tuluol when mixed scarcely change in volume at all, while alcohol and water contract considerably. That is just what would be expected if affinity is the cause of contraction.

In order to use such facts it is not necessary to imagine an atomic theory adapted to them. Such a theory is ventured upon at the end of this paper, but the facts are significant without it. One only has to bear in mind that liquid and solid substances resist compression, and hence that when we find them compressed we have reason to believe that pressure has been applied upon them. It is rather a matter of common sense than a hypothetical abstract conception.

In order to present in a clear light the complications involved in the study of even a simple series of cases of chemical compression, the facts concerning the molecular volumes of several metals and their oxides are recorded and discussed below.

MOLECULAR VOLUMES OF OXIDES.

Substance.	Weight of metal combined with 16 grams oxygen.	Density of metal.	Density of oxide.	Space occupied by given weight of metal.	Space occupied by corresponding weight of oxide.	Excess of volume of oxide.
2 Ag . . .	215.86	10.56	7.521	20.55	31.55	+11.00
Hg	200.00	13.50	11.136	14.71	19.4	+ 4.7
Cu	63.6	8.95	6.40	7.10	12.4	+ 5.3
Ni	58.7	8.9	6.39	6.80	11.75	+ 5.15
Cd	112.3	8.67	6.5	12.95	19.7	+ 6.75
Zn	65.4	6.9	5.6	9.5	14.5	+ 5.0
Mg	24.86	1.74	3.4	14.0	12.0	- 2.0
2 Na . . .	46.1	0.973	2.80	47.4	22.6	-24.8
2 H	2.0	0.07	1.00	28.2	18.0	-10.0
Si	14.2	2.00	2.30	7.1	13.14	+ 6.0

While in the first part of this paper no atomic hypothesis is assumed, the words atomic volume, atomic weight, and atomic heat will be used in a purely material sense, as the actual constants pertaining to quantities chemically consistent.

The results recorded in this table are typical of the variety of degrees of contraction which take place when substances combine with oxygen. It is evident that in some cases the product occupies considerably more space than the metal from which it was formed, and that in others (typified by magnesium and sodium above) the oxide occupies considerably *less* space than the metal. This last remarkable circumstance at once emphasizes the absurdity of estimating the atomic volume of an element in a compound by discovering the volume-change which takes place when that element is replaced by another. Oxygen cannot be said to occupy a *minus* quantity of space,—the only possible outcome of the false assumption in this particular case. The false method gives fairly consistent results among carbon compounds only because of the great similarity of their composition. This consideration leads to the first law underlying the change of volume in chemical or physical change, namely, *The atomic volume is not a constant, but is dependent upon the environment.* This law was first suggested by Horstmann,* but he looked upon it rather as the absence of a law than as the presence of one.

If the affinity of oxygen for the metal were the only variable entering into the figures given above, it is obvious that the total contraction, the difference between the volumes of factors and product, would be at once a comparative measure of the attractive forces which produce the compression. This reasoning of course rests upon the plausible ground that a state of being which resists pressure, such as liquid oxygen or solid metal, may be compressed only by the application of pressure. In this case pressure may be supposed to be applied by the mutual affinity. But unfortunately the case is not so simple.

It is clear that in each case recorded above at least three affinities are concerned: first, the affinity of the metal for itself; second, the affinity of oxygen for itself; and third, affinity of the metal for oxygen. The second of these is constant throughout the series, hence for the present comparison it may be considered as a known quantity. Therefore each change of volume may concern at least two unknown quantities. Hence if it were possible to measure either of the two

* Horstmann, Ostwald's Lehrbuch, I. 389 (1801).

variable affinities, an approximate idea could be obtained concerning the other from these data concerning atomic and molecular volume.

A slight uncertainty is caused also by the possible varying intensity of the "crystal-making tendency" which determines the structure of solids. The small differences caused by this uncertainty may be seen from the following typical calculation. If solid rather than liquid mercury had been chosen above, the atomic volume of the mercury would have become $\frac{200}{14.1} = 14.2$ instead of 14.7, and the excess of volume of the oxide would have been 5.2 instead of 4.7. These differences are unimportant compared with the larger values under consideration; the precise state of the solids or liquids makes less difference than one would have supposed.

Is there any direct method of determining either the mutual affinity of the two elements or the affinity of the metal for itself?

Countless attempts to measure the former have so continually resulted in failure that many chemists are inclined to deny the existence of chemical affinity. The electrometric method suggested by Ostwald* clearly measures one of the ways in which chemical affinity may accomplish work, but it is limited in application and only represents a small fraction of the possibilities. The thermal relations are complicated by well-known thermodynamic irregularities, and would be fully significant only at the imaginary absolute zero.

The direct determination of the affinity of a substance for itself is an easier matter, for many of the properties of a single substance, such as volume, compressibility, tenacity, must be associated with this affinity. Let us seek to study these relationships more closely.

If one could only be sure that all substances, when relieved of their self-affinity, would occupy the same volume, the atomic volume itself would be the simplest and most direct means of comparing this property in different substances. The smaller the actual atomic volume, the greater must be the self-affinity. Such an assumption would at first sight seem to be justified, for those elements which have the largest atomic volumes have the least inclination to remain in the elementary states. Deserting the elementary state means introducing other affinities, however; hence the assumption would be unsafe.

It has been already pointed out that compressibility, if measured over a wide range of pressures, might afford a clue to the extent of compres-

* Ostwald, *The Chemometer*, *Z. phys. Chem.* **15**, 399 (1894).

sion already existing in any given substance. But the comparison of different substances involves the dangerous assumption that all substances would be alike compressible if freed from self-affinity,—an assumption which seems more probable than the last, but which nevertheless must be rejected. A much safer measure of the stress under which a single substance rests is the work which heat is able to do upon it. The changing of a simple substance from t° to $t^{\circ} + dt^{\circ}$ Centigrade must involve the addition to it of an amount of internal work which is represented by the rise of temperature multiplied by the heat capacity of the substance, or $C dt$. In a simple elementary substance, when this work does not involve the alteration of crystalline form or any other apparent change except increase in size, it seems reasonable to consider no other variables, at least as a working hypothesis. If this is the case, we may write $C dt = P dv$, in which P is the internal stress against which the heat-energy is doing work, C the molecular heat capacity, t temperature, and v volume. The stress against which this work is being done is due only to the internal stress and to atmospheric pressure (which latter may be neglected by comparison with the very large value of the former), hence the stress $= P = \frac{C dt}{dv}$. This can apply precisely

only to infinitesimal changes, because in all probability P will vary with the volume. While it cannot be claimed that the expression just given certainly expresses a *single* pressure pitted against temperature-work, the expression certainly represents a *resultant* tendency which opposes expansion by heat, and therefore, by inference, opposes all other forms of expansion.* It is the *inward tendency*, the opposite to the driving tendency† or fugacity.‡

While then this stress, represented by the quotient of energy divided by change of volume, can hardly represent anything very definite, it must nevertheless be supposed in a general way to increase when the self-affinity increases. Hence, while giving no certain knowledge, its study may give an indication of affinity.

A typical comparison may be made of the two elements zinc and mercury. They are simple, similar, and yet widely different as to their power of holding oxygen. In each case the atomic contraction on union with oxygen is about the same. If we take as the atomic volume of

* All the slight data which we possess upon compressibility seem to run parallel with the coefficients of expansion.

† Richards, These Proceedings, 35, 471.

‡ Lewis.

oxygen the atomic critical volume, the contractions are as follows: $14.7 + 24.5 - 19.4 = 19.8$, in the case of mercury, and $9.5 + 24.5 - 14.5 = 19.5$, in the case of zinc. If the metals were originally subject to the same internal stress, we should infer from the similarity of contractions that the affinities concerned in the two cases were about equal. This inference is, however, overthrown by other facts. Both elements have about the same atomic heat capacity, hence no internal rearrangement takes place in one which is not approximated in the other. On the other hand, the increase in atomic volume for a rise of 1° of temperature exhibited by one is much greater than that exhibited by the other.

If a gram atom of one element increases more rapidly in size than the gram atom of another, it is only reasonable to suppose that the heat energy is finding less opposition in the former case. The coefficient of cubic expansion of mercury is 0.000179 at 0°C . and the heat required to raise a gram through 1° is 0.139 joule. With zinc the corresponding numbers are 0.000087 and 0.392.* The respective atomic volumes are 14.7 and 9.5. Substituting these values in the equation we obtain.

$$P_{Hg} = \frac{(200 \times 0.139)}{(14.7 \times 0.000179)} = 106,000 \text{ megadynes per square cm.}$$

$$P_{Zn} = \frac{(65.4 \times 0.392)}{(9.5 \times 0.000087)} = 310,000 \text{ megadynes per square cm.}$$

Both these pressures are very large, for a megadyne exerts on a square centimeter a pressure of almost an atmosphere. As has been said, they signify a resultant tendency which resists expansion.

It is interesting to note that these stresses agree in their indications with the comparison of boiling points and latent heats of evaporation. The boiling point of mercury is 357° C . and that of zinc about 930° C . The latent heat of evaporation of zinc is not known, but there is no reason for believing that in its case Trouton's rule is broken. Hence the criteria all indicate that zinc is harder to dissociate from itself than mercury is.

A comparison of the energy-quotients of several metals, measured in this way, may be of interest.

* All figures not otherwise designated were taken from the tables of Landolt and Börnstein, 1894.

Metal (in order of boiling point).	Boiling point 760 m.m.	Heat capacity (mayers per gram) $\frac{C}{\text{mol. weight.}}$	Cubic coefficient of expansion.	Energy quotient $P = \frac{Cd^2}{\text{atom. expan. megadynes}}$
Mercury . .	357° C = 630° A	0.139	0.00018	106,000
Cadmium .	770° C = 1043° A	0.23	0.000093	214,000
Sodium . .	860° C = 1133° A	1.21	0.00022	53,700
Zinc	930° C = 1203° A	0.392	0.000087	310,000
Copper . . .	unknown	0.375	0.000050	672,000
Magnesium	1100° \pm = 1400° A	1.02	0.000081	224,000
Lead	1400° \pm = 1700° A	0.126	0.000088	162,000
Silicon . .	unknown	0.7	0.0000230	755,000
Diamond .	unknown	0.5	0.0000036	4,900,000

In these figures one may find traces of many properties associated with firmness of structure or intensity of self-affinity. For example, the order of sequence of the energy-quotients agrees essentially with that of tenacity and of hardness. There is some relationship also to boiling points and melting-points, although here there are more exceptions. "Chemical affinity" is so much affected by electrical relations and by atomic volume that one would expect to find regularity only on comparing similar elements. Such comparison (zinc with cadmium, or carbon with silicon) seems to show that the energy-quotient tends to increase with diminishing atomic weight.

Having thus plausible inference, from independent sources, as to the relative values of the compressing agencies existing in metals at the ordinary temperature, it is worth while to study the correction which must be applied to the volume-change exhibited in chemical combination with another element. In zinc the self-affinity is so great (boiling point = 1200° A), and the metal is hence already so compressed, that a given further pressure causes less change in its volume than it would cause in the case of mercury. That is, the mercury contracts more than zinc when it is oxidized. Hence the difference between the volume of the oxide and the volume of the metal gives too low a value for the volume of the combined oxygen in the case of mercury.

Thus the contraction of the *oxygen* is really less in the case of mercuric oxide, although it appears to be the same.

Without going further, one can explain by means of these considerations the behavior of zincic and mercuric oxides when subjected to high temperatures. The sixteen grams of oxygen in mercuric oxide occupies a larger space than an equal weight in the case of zinc, hence one infers that it is less compressed by its affinity, hence the affinity must be less. This smaller affinity should be more easily overcome by rising temperature, a prediction which agrees with facts. *Thus there appears to be in this case a connection between the compression of substances and their tendency to combine one with another.*

The case under consideration is typical. In the case of sodium and magnesium, the affinity of the metal for oxygen is so enormous as to overcome easily the large affinity of the metal for itself, and besides this to compress both metal and oxygen together into a space smaller than that previously occupied by the metal. This fact corresponds with the great difficulty of decomposing sodic and magnesic oxides. Metallic magnesium probably has as energy-quotient a stress more than four times as great as sodium (see table on p. 10); hence the total contraction on combination with oxygen is less than in the case of sodium. Comparison with the cases of mercury and zinc will show that this small contraction does not necessarily conflict with the fact that magnesium decomposes sodic oxide at high temperatures. Again, the contraction involved in the formation of argentic oxide is very slight. In this case the large volume of oxygen is not concealed by the contraction of the metallic element, as it was in the case of mercury, for silver is not particularly compressible. Hence one can infer that the affinity of silver for oxygen is smaller than that of magnesium for oxygen,—an inference which agrees with fact. Moreover, since the relation is nearly additive, that is, neither silver nor oxygen change much in volume on combination, their combination is easily shifted, that is to say, silver oxide is easily decomposed by heat.

Of course many tables comparing the molecular volumes of solids and liquids might be drawn up, since a very great number of specific gravities have been determined. A table containing chlorides of the metals already considered may be of interest.

Here the variations in contraction are less than they were before. Chlorine evidently possesses more equally distributed affinities than oxygen does, and apparently somewhat weaker ones. The two most interesting features of this table, which may be seen without the elimi-

MOLECULAR VOLUMES OF CHLORIDES.

Substance.	Weight of metal combined with 35.5 grams of chlorine.	Density of metal.	Density of chloride.	Volume of given weight of metal.	Volume of corresponding weight of chloride.	Excess of volume of chloride above metal.
Ag	108.	10.56	5.53	10.27	45.90	+15.63
$\frac{1}{2}$ Hg . . .	100.	14.00	5.42	7.80	25.5	+18.2
Hg	200.	14.00	7.10	14.00	33.2	+19.2
$\frac{1}{2}$ Cu . . .	31.8	8.95	3.05	7.10	25.4	+18.3
$\frac{1}{2}$ Co . . .	28.5	9.00	2.94	3.16	21.8	18.64
$\frac{1}{2}$ Cd . . .	56.2	8.67	3.7	6.47	24.8	18.33
$\frac{1}{2}$ Zn . . .	32.7	6.9	2.753	4.75	25.0	+20.25
Mg	12.2	1.74	2.177	7.0	21.95	+15.00
Na	23.05	0.973	2.15	23.7	27.2	+ 4.2
K	39.14	0.875	1.995	45.7	37.8	- 8.4
Rb	85.44	1.52	2.21	56.1	55.0	- 1.0
H	1.01	0.07	1.27	14.1 (?)	28.9	+14.7
Combined with carbon						22.8
Liquid chlorine at -80° (boiling point, 760 mm.) (sp. gr. = 1.66)						21.5
Liquid chlorine at +80° (sp. gr. = 1.20)						29.6

nation of the self-affinities of the several metals, are the small excess in the case of silver, and the larger excess in the case of mercurous chloride. This is quite in accord with the facts; for argentic chloride is more stable than the oxide, and mercurous chloride easily splits into mercuric chloride and mercury.*

The case of the hydroxides is especially interesting.

The density of the hydroxide of zinc has not been accurately determined; indeed the data concerning cobalt, cadmium, and magnesium are not very trustworthy on account of the amorphous condition of most hydroxides. It is interesting to note that in this table, where the substances are arranged in the order of the contraction which ensues when hydroxyl combines with the metal, *should also be arranged in the electro-chemical*

* Richards, These Proceedings, 33, 9 (1897).

MOLECULAR VOLUMES OF HYDROXIDES.

Substance.	Weight of metal combined with 17 grams hydroxy.	Density of metal.	Density of hydroxide.	Volume of given weight of metal.	Volume of hydroxide corresponding.	Excess of volume of hydroxide above metal.
Ag	The hydroxide is exceedingly unstable.					
$\frac{1}{2}$ Hg	It is doubtful if the hydroxide exists.					
$\frac{1}{2}$ Cu	The hydroxide cannot be dried without decomposition.					
$\frac{1}{2}$ Co	28.5	9.	3.597	3.16	12.67	+ 9.51
$\frac{1}{2}$ Cd	56.2	...	4.79	6.47	15.25	+ 8.78
$\frac{1}{2}$ Mg	12.2	...	2.36	7.0	12.90	+ 5.90
$\frac{1}{2}$ Sr	43.83	2.54	3.62	17.3	17.0	- 0.3
Na	23.05	0.973	2.13	23.7	18.80	- 4.9
K	39.14	0.875	2.044	45.7	27.5	-18.2
Hydroxyl in organic compounds						+12.0
Hydroxyl in hydrogen dioxide (sp. gr. = 1.50) . . .						11.4

order. That is to say, the solution tension of a metal appears to be associated with the excess of affinity of the metal for hydroxyl over its affinity for itself, and intensity of potential seems to be associated with intensity of atomic compression. The inference to be drawn from this comparison is of course that the formation of the metallic ion in water is connected with the affinity of the metal for water,—an affinity which manifests itself even when both of the "bonds" of oxygen are filled.* Similar attraction for nitrogen or sulphur would explain cases in which the solvent does not contain oxygen.

If this is true, contraction should take place when salts are dissolved in water. This inference is amply verified by facts. In some cases the solution occupies even less space than the water alone, involving a total contraction greater than the volume of the salt itself. The best known of these cases are those of lithic, sodic, and baric hydroxides, and

* Brühl has suggested that oxygen is the cause of dissociation, but he ascribes it rather to quadrivalence than to a general affinity.

cobalt, nickel, zinc, and magnesium sulphates,* but undoubtedly others exist. In a large majority of cases when an electrolyte is dissolved in water, the sum of the volumes of salt and of the solvent taken together considerably exceeds the volume of the solution. This contraction is usually ascribed wholly to the dissolved substance in dilute solutions,† but it seems to me that the behavior of the salts named above proves the falsity of this method of calculation. *The water as well as the salt must contract when a salt is dissolved.* So many complications are concerned in the act of the solution of an electrolyte that it is difficult to unravel the tangled clues; but the wide deviations exhibited by different substances seem to indicate that there are present overlapping contractions and expansions, the resultant of which is a smaller quantity than some of the individual influences. Such contractions and expansions are just what one would expect to find in a readjustment of affinities.

In considering the simpler case of solid non-electrolytes, one usually finds here also a contraction upon solution, although less marked than in the extreme cases named above. For this reason, one is inclined to ascribe the act of solution of all kinds primarily to the affinity of the solvent for the dissolved substance. The solution tension of a metal or salt becomes simply a balance or ratio of attractions,—the separating tendency of heat upon the dissolving phase is much assisted by the attraction from outside. This is of course no new idea. The possible method of treating mathematically these balanced influences is suggested in a recent paper on the "driving tendency" of reaction.‡

That electrolytic separation also should be assisted by the outside attraction for the solvent is almost a foregone conclusion. This may be inferred from the contraction shown by most electrolytes on dissolving. Hence may arise the various contact-potentials exhibited by the same substance in different solvents; for different solvents must possess different affinities. Hence also one would expect to find a much greater potential needed for the dissociation of gases than for that of dissolved substances.

The mechanism of electrolytic dissociation in gases is now usually

* Thomsen, *Thermochemische Untersuchungen*, I. 45 (1882). MacGregor, *Trans. Roy. Soc. Canada*, 1890, p. 19; 1891, p. 15; *Trans. Nova Scotia Inst. Nat. Sc.*, 7, 368 (1890).

† Van't Hoff, *Vorlesung phys. theoret. Chem.*, III. p. 41 (1900). Drude and Nernst (*Z. phys. Chem.*, 15, 79 (1896)) ascribe this contraction to "Electrostriction."

‡ Richards, *Jour. Phys. Chem.*, 4, 385 (1900). See specially p. 391.

explained by the aid of the ingenious hypothesis of "electrons," as amplified by J. J. Thomson and his students in the brilliant experimental researches published in the recent volumes of the Philosophical Magazine. This daring hypothesis must not be accepted without reservation, however. Some physical objections to it have been suggested by Ernest Merritt in his interesting address to the American Association for the Advancement of Science;* and other objections arise when one tries with its aid to unravel the tangle of influences involved in purely chemical action. The rejected alternative of imagining the atom as indivisible, but as capable of receiving widely varying electric charges under widely different conditions, has some advantages which the opposite hypothesis does not possess. The subject is much too large for discussion here, however. One phase of it, which bears directly upon the subject of the present paper, may receive brief notice.

The results of Thomson, Townsend, Zeleny † and others seem to indicate that the bearer of the negative electricity not only carries the high charge referred to above, but that it is very small, while the bearer of the positive electricity is very large. May it not be the atom itself which thus expands and contracts? This agrees with the verdict of the results of atomic compression given above. Change of atomic volume seems to be associated with electric stress. This assignment of electric expansibility to the atomic sphere of influence might explain other phenomena concerning the behavior of electrified gases, for example, the increase of pressure which is observed when a gas is highly charged.‡ Again, the great conductivity of a gas with adequate potential and quantity of electrical discharge § seems to indicate that then the situation must resemble that in a metal, where the spheres of stress fill the whole volume occupied by the substance. The temperature must be so high under these circumstances that the gas is probably in a condition of thermal dissociation. Hence one is inclined to refer the great conductivity to the electrical susceptibility of evenly compressed or *undistorted* atoms. The fact that pure metals conduct electricity better than alloys or compounds seems to support this conclusion. The permeability of solids to cathode rays might be explained by supposing that the smallest particles of both solid and gas are much contracted by the negative charge.

* Proc. Am. As. Adv. Soc., 1900, p. 49.

† Phil. Mag. [5] 46, 120, (1898). See also Am. Chem. Journ., 25, 340 (1901), for a résumé of this work.

‡ De la Rue and Müller, Phil. Trans., 1880, 86.

§ Trowbridge and Richards, Phil. Mag. [5] 43, 349 (1897).

It is with some diffidence that this paper attempts to reconcile the facts with any hypothesis, for hypotheses sometimes lead to dangerous delusions. If, however, one never forgets the essential difference between fact and hypothetical inference, a theory may afford useful suggestions for further research. The facts under discussion in the present paper seem to me to be adequately connected by none of the current conceptions concerning atoms, hence it has seemed not wholly pointless to postulate a theory which might serve better. The essential elements of this theory must be evident from the trend of the hypothetical discussion above; they are not wholly new. Since changes of atomic volume seem to be so closely associated with the most intimate properties of substance, it seems necessary to assign more importance to the atomic "sphere of influence" or the "free space" around the atomic centres than is customary. Indeed, the properties of material seem to be as much concerned with the "atomic shell" as with the "atomic centre." The two hypothetical conceptions are so closely related as to be inseparable.

Such a point of view leads to the conception of an atom as a compressible field of force possessing two attractive attributes, chemical affinity and gravitation, both of which may be concerned in chemical action. Mass may be supposed to be causally connected with gravitation. The fact that in many cases affinity diminishes with increasing atomic weight,* taken together with the Laws of Faraday and of Dulong and Petit, suggests that the two attractive forces in the atom may bear some sort of reciprocal or additive relationship to one another,—that the product or sum of the two may afford a constant basis for the vibrations of heat and electricity. This relation is often hidden by electrical attraction, which plays so important a rôle in chemical action that it is sometimes hard to distinguish the intensity of chemical affinity proper. In such an atom one can imagine that either thermal or electrical vibration might cause distention. The phenomena of electricity suggest that electricity plays around the atomic surface, while heat seems to be concerned with a more fundamental or central agitation. Light-vibration, which seems also to be intimately concerned with atomic structure, would be assumed to be a surface effect like electrical vibration.

Such an atom would be compressible under the influence of its own affinities as well as under the influence of external pressure. Permanent

* Van't Hoff, Vorl. th. phys. Chem., III. 87 (1900). Compare also the relation of the energy-quotients of similar metals referred to on p. 10 of the present paper.

atomic distortion would accompany chemical union, and the heat of the reaction would be the outcome of the resulting decrease of internal energy. Atomic volume and atomic compressibility might limit the possibility of distortion; hence would arise a possible explanation for quantivalence, stereochemistry, and crystal form. Many other properties of material, too numerous to mention, seem to be explicable in a similar way.

It would be unreasonable to expect the hypothesis thus briefly described to correspond to all known facts. No hypothesis has ever been proposed which is wholly satisfactory; our knowledge is incommensurate with the possibilities involved. If, however, a given theory is found to explain some relationships better than other hypotheses, it may be of service in suggesting new experimental research. Such a service is of course the best one which a hypothesis can perform.

The idea discussed above has been already applied in plausible fashion to a wide range of chemical and physical phenomena. If future experimentation to be carried on here seems to warrant it, these applications may form the subject of another communication.

The object of the present paper may be summed up in a few words, as follows: It is pointed out that changing atomic volume may be used as an approximate measure of the pressure which causes it, and therefore of the affinity which causes the pressure. Some of the difficulties in the way of exact interpretation are pointed out, and hints are given as to possible modes of overcoming the difficulties.

The chief outcome of the paper is the following postulate: *The atomic volume is not constant, but a function of pressure and temperature, and probably of electric stress.*

In this connection it is pointed out that chemical affinity is possibly a reciprocal function of mass.

To explain these and many other facts, a modification of the atomic hypothesis is tentatively proposed which contends that we have no right to disregard the compressible environments around the centres of gravity and affinity.

CAMBRIDGE, MASS.